Chemical equilibrium of esterification in AcOH—EtOH—H_2O—EtOAc system at 293.15 K

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New experimental data on the chemical equilibrium of esterification in an acetic acid—ethanol—water—ethyl acetate system at 293.15 K and atmospheric pressure are presented.

Key words: chemical equilibrium, esterification, ethyl acetate.

Thermodynamic investigation of multicomponent systems with chemical reaction is one of the modern directions of thermodynamics of heterogeneous systems. The study of phase equilibria in reaction systems, predominantly the simultaneously existing chemical equilibrium and vapor—liquid equilibrium, is central in this research.[1—5] This direction of research is related, in particular, to significance of reaction mass exchange processes for chemical technology and organization of combined and hybrid processes. One of examples for processes of this type is reactive distillation.[1,2,6—8] Nevertheless, the database on the chemical equilibrium itself in multicomponent systems is presently restricted. This is possibly associated with time-consuming detailed studies of chemical equilibrium even in the systems consisting of four substances, because the full representation of chemically equilibrium compositions requires the construction of the equilibrium surface in a concentration tetrahedron. This problem can be solved only as a result of prolong experiment on the determination of at least 50 chemically equilibrium compositions.

In this work, we present the experimental data on the chemically equilibrium compositions in the four-component acetic acid—ethanol—water—ethyl acetate system at 293.15 K. This system has earlier been studied experimentally at other temperatures or for restricted concentration ranges (see review[5]). In particular, the experimental results were obtained for a temperature of 343.15 K,[9] a pressure of 101.3 kPa,[10] and atmospheric pressure.[11] The model calculations were also presented (see review[5]), for example, in the framework of the UNIQUAC model at atmospheric pressure.[12]

In this report we confine ourselves to presenting chemical equilibrium surface on the basis of the obtained experimental data. The determination of thermodynamic constants of chemical equilibrium demand additional experiments, for example, studies on equilibrium with vapor or model calculations.

Experimental

Experiments were carried out taking into account a series of requirements imposed on the choice of the initial compositions of the solutions. Compositions of chemically nonequilibrium solutions were chosen in such a way that the concentrations of the final chemically equilibrium mixtures would maximally completely reflect the arrangement of the chemical equilibrium surface in the concentration tetrahedron. In other words, figurative points of equilibrium phases should uniformly be arranged on this surface. To save experimental time, four-component nonequilibrium mixtures corresponding to the compositions in the vicinity of the assumed chemical equilibrium were prepared in most cases.

Ethanol (pure) and ethyl acetate (reagent grade) were predistilled on a rectification column with an efficiency of ~17 theoretical plates. Acetic acid (reagent grade) was purified by double rectification in the presence of sulfuric acid (98%). Bidistilled water was used. Purity of the substances was controlled chromatographically, by the refractive indices and boiling points; the purity was at least 0.995 molar fractions. The physicochemical constants of the pure substances corresponded to the literature data.[13]

The initial reaction mixtures were prepared on a Shinko VIBRA HT-120CE analytical balance (Japan) (weighing accuracy 0.0001 g). The catalyst (0.035 g ("one droplet") of 36.5% HCl) was added to the reaction mixture (volume ~3.5 mL). The mixture was kept in a TZh—TS—01 liquid thermostat at 293.15±0.05 K and atmospheric pressure until the chemical equilibrium was attained.

The criterion of achievement of chemical equilibrium for esterification was invariability of the component concentrations in the studied sample for several days. The time of chemical equilibration at 293.15 K in the presence of the catalyst was 45 days on the average. After chemical equilibration, samples (1 or 10 μL in volume) were taken with a Hamilton chromatographic syringe and injected into the chromatograph.

Compositions of chemically equilibrium phases were determined by gas chromatography on a Kristall 5000.2 chromatograph. The separation parameters were as follows: a Porapac R packing column (length 1 m, inner diameter 3 mm), helium

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(trade mark A) as a carrier gas, and a flow rate of 30 mL min^{-1}. The working temperature of the columns was ~453 K, that of the heat conductivity detector was 513 K, and the evaporator temperature was 503 K. Ethanol was accepted as a cross-linking component when determining the compositions of the mixtures using the internal standard method and relative calibration. Each sample was analyzed 2—3 times; the error of gas chromatographic analysis was ±0.005 molar fractions on the average.

Results and Discussion

The experimental data on the chemical equilibrium in the acetic acid—ethanol—water—ethyl acetate system at 293.15 K and atmospheric pressure are listed in Table 1 along with the values of empirical (concentration) equilibrium constant (K')

$$K' = \frac{x_w x_e}{x_{ac} x_{et}},$$

where x_{ac}, x_{et}, x_w, and x_e are the molar fractions of the acid, ethanol, water, and ester, respectively, for each chemically equilibrium composition. These data show how K' varies with changing concentration, *i.e.*, with moving composition along the chemical equilibrium surface. The highest values of K' are observed in the region of chemical equilibrium surface corresponding to high water concentrations, and the lowest K' values are observed at low concentrations. Figure 1 shows that the chemical equilibrium surface in the composition space is a distorted tetrahedron. In this case, the points of chemically equilibrium compositions can be specified in the rectangular Cartesian crossbar system. According to the stoichiometric equation of the reaction

$$MeCOOH + MeCH_2OH = H_2O + MeCOCH_2Me, \quad (1)$$

all four ternary subsystems of the four-component system can be in the chemically nonequilibrium state only. Two binary systems, namely, acetic acid—ethanol and water—ethyl acetate, are also chemically nonequilibrium. Therefore, the chemical equilibrium surface cannot belong to faces and edges of the composition tetrahedron corresponding to the indicated ternary and binary subsystems. In other four binary subsystems (acetic acid—ethyl acetate, acetic acid—water, ethanol—water, and ethanol—ethyl acetate), no chemical reaction occurs and, hence, the corresponding edges of the concentration tetrahedron should be considered as boundaries of the chemical equilibrium surface. The same is valid for the vertices of the tetrahedron: points corresponding to neat substances. Thus, the chemical equilibrium surface is arranged inside the composition tetrahedron and is based on four edges corresponding to the binary systems without chemical reactions.

The arrangement of the chemical equilibrium surface is typical of similar thermodynamic surfaces in the systems of ester synthesis.[5,14—16] The data of Table 1 provide

Table 1. Equilibrium compositions of the acetic acid—ethanol—water—ethyl acetate system at 293.15 K and atmospheric pressure and empirical equilibrium constants (K')

Concentration/mol. fractions				K'	Concentration/mol. fractions				K'	Concentration/mol. fractions				K'
AcOH	EtOH	H_2O	EtAcO		AcOH	EtOH	H_2O	EtAcO		AcOH	EtOH	H_2O	EtAcO	
0.065	0.093	0.761	0.081	10.20	0.135	0.143	0.520	0.202	5.44	0.217	0.120	0.401	0.262	4.03
0.096	0.148	0.480	0.276	9.34	0.654	0.008	0.141	0.197	5.31	0.295	0.082	0.255	0.368	3.88
0.763	0.002	0.103	0.132	8.91	0.285	0.065	0.412	0.238	5.29	0.034	0.356	0.520	0.090	3.86
0.197	0.056	0.577	0.170	8.91	0.533	0.018	0.257	0.192	5.14	0.190	0.062	0.066	0.682	3.82
0.100	0.132	0.573	0.195	8.46	0.027	0.338	0.553	0.082	4.97	0.112	0.169	0.600	0.119	3.78
0.070	0.104	0.745	0.081	8.28	0.336	0.054	0.374	0.236	4.86	0.672	0.010	0.148	0.170	3.74
0.837	0.001	0.097	0.065	7.53	0.439	0.033	0.261	0.267	4.83	0.133	0.148	0.598	0.121	3.68
0.113	0.081	0.711	0.095	7.38	0.445	0.026	0.141	0.388	4.73	0.083	0.190	0.636	0.091	3.66
0.170	0.079	0.583	0.168	7.29	0.602	0.013	0.198	0.187	4.73	0.128	0.208	0.445	0.219	3.65
0.393	0.028	0.379	0.200	6.89	0.291	0.055	0.505	0.149	4.70	0.273	0.099	0.366	0.262	3.55
0.102	0.146	0.586	0.166	6.53	0.495	0.022	0.326	0.157	4.69	0.128	0.143	0.105	0.624	3.55
0.188	0.099	0.435	0.278	6.48	0.344	0.044	0.458	0.154	4.65	0.083	0.298	0.399	0.220	3.55
0.255	0.058	0.497	0.190	6.38	0.361	0.046	0.190	0.403	4.63	0.637	0.014	0.178	0.171	3.41
0.162	0.091	0.588	0.159	6.34	0.304	0.071	0.316	0.309	4.52	0.199	0.144	0.430	0.227	3.40
0.634	0.008	0.195	0.163	6.30	0.043	0.359	0.440	0.158	4.50	0.159	0.190	0.395	0.256	3.34
0.413	0.031	0.307	0.249	5.97	0.036	0.307	0.570	0.087	4.49	0.042	0.450	0.305	0.203	3.28
0.638	0.007	0.105	0.250	5.88	0.221	0.113	0.353	0.313	4.42	0.088	0.361	0.327	0.224	2.31
0.346	0.041	0.199	0.414	5.81	0.422	0.037	0.351	0.190	4.27	0.097	0.314	0.322	0.267	2.82
0.570	0.012	0.278	0.140	5.69	0.590	0.015	0.234	0.161	4.26	0.027	0.645	0.167	0.161	1.54
0.251	0.059	0.534	0.156	5.63	0.532	0.020	0.292	0.156	4.28	0.012	0.357	0.004	0.627	0.73
0.173	0.123	0.429	0.275	5.54	0.047	0.372	0.403	0.178	4.10					
0.561	0.011	0.106	0.322	5.53	0.130	0.115	0.663	0.092	4.08					

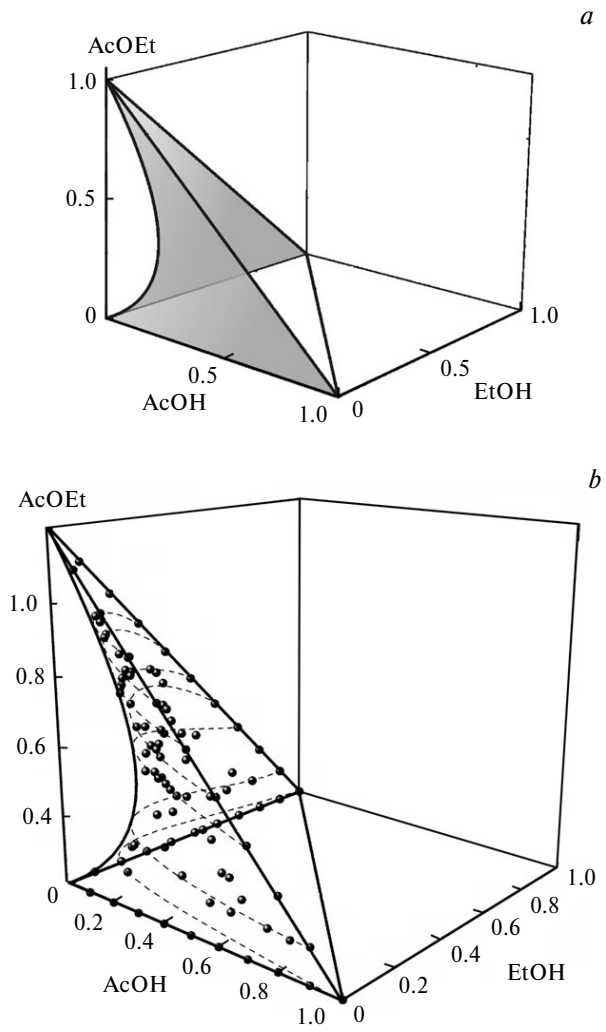

Fig. 1. Chemical equilibrium surface in the acetic acid—ethanol—water—ethyl acetate system at 293.15 K and atmospheric pressure: *a*, general view of the chemical equilibrium surface; *b*, figurative points of experimentally determined chemically equilibrium compositions on the surface.

information on the chemically equilibrium compositions and allow one to estimate the conversion of the substances and the yield of the final esterification product at different initial compositions of binary or ternary reaction systems. In the case of the synthesis of ethyl acetate, these are the acid—alcohol system and the ternary systems acid—alcohol—water and acid—alcohol—ester.

Thus, the experimental data obtained fairly completely describe the chemical equilibrium in the acetic acid—ethanol—water—ethyl acetate system at 293.15 K for all possible ranges of compositions of the reaction mixtures. These data can be useful for the development of the thermodynamic theory of chemical equilibrium in multicomponent systems and for studies of topology of diagrams of reaction systems. The results of the work are interesting in the practical aspect as well: they can be useful in manufacturing of ethyl acetate in the basic organic synthesis.

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